ammonium hydroxide of the inner bark of the black spruce (*Picea mariana* B. S. P.) and of holocellulose from the inner bark.[7] It was precipitated as calcium pectate. By treatment with hydrochloric acid the calcium pectate was converted to an impure pectic acid with $[\alpha]^{20}\text{D}$ +80° (3% NaOH) and containing 66.5% uronic anhydride (on an oven-dry basis).

A control experiment using commercial pectic acid[8] containing 77% uronic anhydride gave sodium calcium galacturonate in 53% of the theoretical yield.

The hydrolyses were carried out according to the directions of Isbell and Frush[6] except that: (1) an aqueous dispersion of pectic acid was treated with sodium bicarbonate until the *p*H was 3.8; (2) the hydrolysis time was twelve days at 38°; 12 g. of pectic substance (oven-dried) was used.

From 13 g. of wood pectic material (containing 11% moisture) 3.1 g. of sodium calcium D-galacturonate $[NaCa(C_6H_9O_7)_3 \cdot 6H_2O]$ was obtained; this yield is 28% of the theoretical value. The equilibrium specific rotation in 0.1 *N* nitric acid was $[\alpha]^{20}\text{D}$ +43.4 (*c*, 2%), whereas Isbell and Frush reported $[\alpha]^{20}\text{D}$ +44.0. The product contained 5.26% calcium; this value compares with 5.35% calculated for the above formula.

When 0.601 g. of the above product was dissolved in dilute hydrochloric acid and treated with bromine for four hours at room temperature 0.257 g. of insoluble material separated. A further crop of 0.066 g. was obtained from the mother liquor. The melting point of the material was 208–210° (dec.). Upon the basis of the insolubility and melting point the material must be mucic acid. The yield was 64% of the theoretical value.

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[8] California Fruit Grower Exchange, Ontario, Cal.

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Trimethylhalosilane Preparations[1]

BY B. O. PRAY,[2] L. H. SOMMER, G. M. GOLDBERG, G. T. KERR, P. A. DI GIORGIO[3] AND F. C. WHITMORE

Previously reported preparations of trimethylfluorosilane have utilized the reaction of trimethylchlorosilane with zinc fluoride,[4] and with antimony trifluoride in the presence of antimony pentachloride.[5]

We have found that trimethylfluorosilane can be prepared directly in about 80% yield by the addition of ammonium fluoride to a solution prepared from hexamethyldisiloxane and concentrated sulfuric acid.[6]

$$(CH_3)_3SiOSi(CH_3)_3 \xrightarrow[H_2SO_4]{NH_4F} 2(CH_3)_3SiF$$

A similar procedure, using ammonium chloride, constitutes an excellent method for the preparation of trimethylchlorosilane in good yield (85%) and high purity. This method for trimethylchlorosilane gives better yields and is more convenient than that involving reaction of methylmagnesium halide with silicon tetrachloride.[7] The latter forms an azeotrope with trimethylchlorosilane[8] and careful fractionation is required to effect separation from dimethyldichlorosilane and methyltrichlorosilane which are also formed.[7] The present method gives only trimethylchlorosilane. Thus, hexamethyldisiloxane is a convenient starting material for three of the trimethylhalosilanes.[9]

In the present work, trimethylbromosilane[9] and trimethyliodosilane have been prepared by fission of the phenyl–silicon bond in phenyltrimethylsilane with bromine and iodine, respectively.[10]

$$C_6H_5Si(CH_3)_3 \xrightarrow{X_2} C_6H_5X + (CH_3)_3SiX$$

The above synthesis of trimethyliodosilane completes the series of trimethylhalosilanes. Trimethyliodosilane is a colorless liquid which fumes vigorously in moist air and acquires an iodine color on standing.

Experimental

Hexamethyldisiloxane from Ethyl Orthosilicate.[11]—Ethyl orthosilicate, 8.7 moles, was added with vigorous stirring during thirty minutes to 28 moles of methylmagnesium bromide in 12 liters of ether while keeping the reaction mixture at 10°. Stirring and cooling were continued for one hour followed by refluxing for two hours. Ether and product were then distilled. After removal of the ether, the product was dissolved in 700 cc. of concentrated sulfuric acid, and the resulting solution was added to ice. Fractionation of the upper layer, after washing and drying, gave 380 g. (2.35 moles) of hexamethyldisiloxane, b. p. 99–100°, $n^{20}\text{D}$ 1.3771, 54% yield.

Trimethylfluorosilane.—Ammonium fluoride, 24.2 g. (0.7 mole) was added from a dropping bottle to a stirred ice-cold solution of 32.4 g. (0.2 mole) of hexamethyldisiloxane in 60 cc. of concentrated sulfuric acid during one hour. Warming gave 31 g. of distillate of clear colorless liquid. Fractionation gave 3.2 g., b. p. 15.4°, and 27.8 g., b. p. 15.8° at 734 mm., of pure trimethylfluorosilane.

Anal. Calcd. for C_3H_9SiF: F, 20.6. Found: F, 20.3, 20.4.

A molecular weight determination by the vapor density method gave mol. wt. 92 (calcd. 94).

Trimethylchlorosilane.—Dry powdered ammonium chloride, 321 g. (6 moles), was added during three hours with vigorous stirring to a solution prepared from 324 g. (2 moles) of hexamethyldisiloxane and 1000 g. of concentrated sulfuric acid. During the addition the flask was cooled in an ice-bath. Upon completion of the addition, *the upper layer was separated as quickly as possible.* Fractional distillation gave 369 g. (3.4 moles) of trimethylchlorosilane, b.p. 58° (734 mm.), $n^{20}\text{D}$ 1.3884, d^{20} 0.8581, a yield of 85%.

Trimethylbromosilane.—Using the method of Bygden,[12] phenyltrimethylsilane, b. p. 168 (734 mm.), $n^{20}\text{D}$ 1.4900, was prepared in 72% yield by the reaction of phenyltrichlorosilane with methylmagnesium bromide. Liquid bromine, 162 g. (1 mole), was added with stirring to 150 g. (1 mole) of phenyltrimethylsilane in a flask cooled with cold tap-water, and the reaction mixture was heated on the steam-bath for one hour. Fractional distillation gave

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[1] Paper XI in a series on organsilicon compounds; paper X, THIS JOURNAL, **69**, 2108 (1947).

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[4] Newkirk, THIS JOURNAL, **68**, 2736 (1946).

[5] Booth and Suttle, *ibid.*, **68**, 2658 (1946).

[6] *Cf.* Flood, *ibid.*, **55**, 1735 (1933).

[7] Gilliam and Sauer, *ibid.*, **66**, 1793 (1944).

[8] Sauer, U. S. Patent 2,381,139, *C. A.*, **39**, 4890 (1945).

[9] The preparation of trimethylbromosilane from hexamethyldisiloxane has been reported by Gilliam, Meals and Sauer, THIS JOURNAL, 1161 (1946).

[10] Grüttner and Cauer, *Ber.*, **51**, 1289 (1918), have reported a similar fission of *p*-di-(triethylsilyl)-benzene with bromine.

[11] *Cf.* Daudt, U. S. Patent 2,386,441; *C. A.*, **40**, 1866 (1946).

[12] Bygden, *Ber.*, **40**, 2274 (1907).

130 g. (0.85 mole) of trimethylbromosilane,[9] b. p. 79° (744 mm.), a yield of 85%, and 130 g. (0.84 mole) of bromobenzene. The bromosilane was analyzed for bromine content.

Anal. Calcd. for C_3H_9SiBr: Br, 52.3. Found: Br, 52.3, 52.3.

Trimethyliodosilane.—In a 500-cc. round-bottomed flask there were placed 75 g. (0.5 mole) of phenyltrimethylsilane and 127 g. (0.5 mole) of iodine crystals. After refluxing the reaction mixture for twelve hours, unreacted iodine was removed by adding 15 g. of powdered antimony. Fractional distillation gave 56 g. (0.28 mole) of trimethyliodosilane, b. p. 106.5° (734 mm.), d^{20} 1.47, a yield of 56%.

Anal. Calcd. for C_3H_9SiI: I, 63.5. Found: I, 63.0, 62.8.

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Competitive Reactions between Trialkylchlorosilanes and Alkylmagnesium Bromides[1]

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In connection with studies in the chemistry of trialkylsilyl compounds, it was of interest to determine the effect of structural variations on the reactivity of trialkylchlorosilanes with alkylmagnesium bromides. Three studies of this type are reported in the present paper.

In one experiment, methyl- and ethylmagnesium bromides, 0.42 mole of each, were allowed to compete for 0.42 mole of triethylchlorosilane. The latter reacted exclusively with the methylmagnesium bromide.

$$CH_3MgBr + C_2H_5MgBr + (C_2H_5)_3SiCl \longrightarrow (C_2H_5)_3SiCH_3 \quad (1)$$

This result is in line with the generally observed greater reactivity of the shorter-chain aliphatic Grignard reagents with purely organic compounds.[2]

Treatment of a mixture of trimethylchlorosilane and triethylchlorosilane, 0.5 mole of each, with ethylmagnesium bromide, 0.5 mole, gave ethyltrimethylsilane and tetraethylsilane in a mole ratio of approximately 2 to 1.

$$2(CH_3)_3SiCl + (C_2H_5)_3SiCl + 3C_2H_5MgBr \longrightarrow 2(CH_3)_3SiC_2H_5 + (C_2H_5)_4Si \quad (2)$$

n-Propylmagnesium bromide, which is generally less reactive than ethylmagnesium bromide, gave stronger emphasis to the difference in the reactivity of trimethyl- and triethylchlorosilane. No appreciable amount of *n*-propyltriethylsilane was found.

$$(CH_3)_3SiCl + (C_2H_5)SiCl + C_3H_7MgBr \longrightarrow (CH_3)_3SiC_3H_7 \quad (3)$$

In general, the decreased activity toward Grignard reagents with increased size of the alkyl groups on silicon, as in reactions 2 and 3, is paralleled by a similar change in reactivity with structure of other trialkylsilyl compounds toward other reagents. For example, trimethylsilanol is far more susceptible toward intermolecular dehydration to the disiloxane than is triethylsilanol.[3]

Experimental

Reaction of Triethylchlorosilane with Methyl- and Ethylmagnesium Bromides.—In a 3-liter, three-necked flask, fitted with a mercury-sealed stirrer, a reflux condenser and a separatory funnel, were placed 139 cc. (0.42 mole) of methylmagnesium bromide and 165 cc. (0.42 mole) of ethylmagnesium bromide. To a mixture of Grignard reagents in ether solution was added, during fifteen minutes, with stirring and cooling, 63.0 g. (0.42 mole) of triethylchlorosilane. The mixture was refluxed for four hours, and then the reaction flask was fitted with a condenser for distillation of material volatile at steam-bath temperature. Completion of the distillation after four hours was followed by heating of the residue on the steam-bath for eight hours. The distillate was then returned to the flask, and 500 cc. of water was slowly added with stirring in order to decompose unreacted Grignard reagent. The resulting product was steam-distilled, the organic layer was separated and the aqueous layer extracted with 65 cc. of ether. Ether was removed from the product by distillation and the residue was refluxed with dilute hydrochloric acid for eight hours in order to convert any triethylsilanol (from the hydrolysis of unreacted triethylchlorosilane) to hexaethyldisiloxane. The organic layer was separated, washed free of acid, and dried over anhydrous magnesium sulfate. Fractionation in a glass-helix packed column of about 20 theoretical plates gave 36.1 g. (0.28 mole) of methyltriethylsilane,[4] b. p. 126° (729 mm.), $n^{20}\text{D}$ 1.4160, and no tetraethylsilane.

Reaction of Ethylmagnesium Bromide with Trimethyl- and Triethylchlorosilanes.—Addition of a mixture of trimethyl- and triethylchlorosilane (0.5 mole of each) to ethylmagnesium bromide (0.5 mole) was followed by a treatment similar to that employed above. Fractionation gave: 18.3 g. (0.18 mole) of ethyltrimethylsilane,[4] b. p. 62° (734 mm.), $n^{20}\text{D}$ 1.3819–1.3821, and 13.6 g. (0.095 mole) of somewhat impure tetraethylsilane,[4] b. p. 152–156° (734 mm.), $n^{20}\text{D}$ 1.4259–1.4245. In addition, there were obtained 18.5 g. (0.091 mole) of 1,1,1-trimethyl-3,3,3-triethyldisiloxane,[5] b. p. 172° (724 mm.), $n^{20}\text{D}$ 1.4104 and 25.1 g. (0.101 mole) of hexaethyldisiloxane,[6] b. p. 128° (30 mm.), $n^{20}\text{D}$ 1.4335.

Reaction of *n*-Propylmagnesium Bromide with Trimethyl- and Triethylchlorosilanes.—Addition of a mixture of trimethyl- and triethylchlorosilane (0.5 mole of each) to *n*-propylmagnesium bromide (0.5 mole) was followed by treatment of the reaction mixture in a manner similar to that above, except that the crude reaction product was treated with 50 cc. of cold concentrated sulfuric acid prior to fractionation in an attempt to separate tetraalkylsilane, which is known to be insoluble in concentrated sulfuric acid, from the disiloxanes which are soluble. The upper layer, containing tetraalkylsilane, was washed free of acid with water and sodium bicarbonate solution, and was then dried with anhydrous sodium sulfate. Fractionation of the product gave 33.3 g. (0.287 mole) of *n*-propyltrimethylsilane,[4] b. p. 89° (729 mm.), $n^{20}\text{D}$ 1.3930, and no appreciable quantity of *n*-propyltriethylsilane. In addition, there was obtained 22.1 g., (0.090 mole) of hexaethyldisiloxane, b. p. 129° (30 mm.), $n^{20}\text{D}$ 1.4340.

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[1] Paper XII in a series on organosilicon compounds; for Paper XI see THIS JOURNAL, **69**, 433 (1947).

[2] Gilman, St. John, St. John and Lichtenwalter, *Rec. trav. chim.*, **55**, 577, 588 (1936).

[3] Sauer, THIS JOURNAL, **66**, 1707 (1944); Sommer, Pietrusza and Whitmore, *ibid.*, **68**, 2282 (1946).

[4] Whitmore, Sommer, Di Giorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, THIS JOURNAL, **68**, 475 (1946).

[5] Sauer, *ibid.*, **68**, 954 (1946).

[6] Di Giorgio, Strong, Sommer and Whitmore, *ibid.*, **68**, 1380 (1946).